

Direct Evidence of the Hydrogen Atom Transfer in Methyl Salicylate in the Triplet State

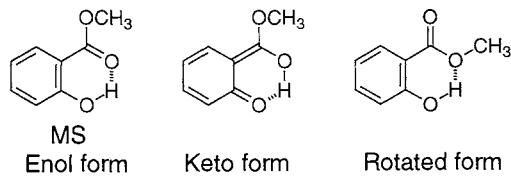
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Intramolecular hydrogen atom transfer in the triplet state of methyl salicylate has been studied by means of transient absorption spectroscopy. Based on the results, it has been revealed that methyl salicylate forms the keto form in the triplet state.

Methyl salicylate (MS) has been well known to undergo intramolecular hydrogen atom transfer (or proton transfer) in the excited singlet state. Steady-state¹⁻¹⁵ and time resolved⁶⁻¹⁵ fluorescence spectroscopies have revealed the dynamics of hydrogen atom transfer reaction in MS. MS exhibits the dual fluorescence in polar solvents. The UV emission ($\lambda_{\text{max}} = 360$ nm) is assigned to the rotated form with a weak intramolecular hydrogen bond between the phenol hydrogen and the methoxy oxygen of the ester moiety,⁶⁻¹⁵ and the blue emission ($\lambda_{\text{max}} = 450$ nm) is due to the keto form generated via the excited state intramolecular hydrogen atom transfer reaction.



Although a lot of extensive studies of the dynamics of the hydrogen atom transfer reaction in the excited singlet state have been reported, only a few has been reported about the behavior of MS in the triplet manifold.¹⁶⁻¹⁸ Previously, Catalán and Díaz have studied the external heavy atom effect on the phosphorescence of MS at 77 K using ethyl iodide matrices and they have showed that the phosphorescence peaked at 560 nm has been assigned to the emission from T_1' state.¹⁶ In order to ensure the formation of the keto form in the triplet state, we applied the quenching experiments similar to that we have carried out to investigate the hydrogen atom transfer of 2'-hydroxychalcone.¹⁹

In this letter, we report the first direct evidence of the intramolecular hydrogen atom transfer reaction of MS in the triplet state. MS forms keto form in the triplet state in benzene at room temperature on direct irradiation as well as triplet sensitization.

Figure 1 shows the transient absorption spectra of MS in benzene on excitation in the presence of acetophenone ($E_T = 310$ kJ mol⁻¹)²⁰ as a triplet sensitizer exciting at 360 nm laser pulse. The transient with the absorption maximum at ca. 450 nm decayed with the lifetime of 4.0 μ s in benzene. The same transient spectra was observed on direct excitation with 308 nm excimer laser under Ar about 500 ns after excitation. The transient was quenched by oxygen and assigned to the triplet state; the quenching rate constant was determined to be 2.8×10^9 M⁻¹ s⁻¹ in benzene. The enol form, the keto form, or the rotated form can be the candidates for the triplet transient. In order to make clear the conformation of the observed triplet state, triplet

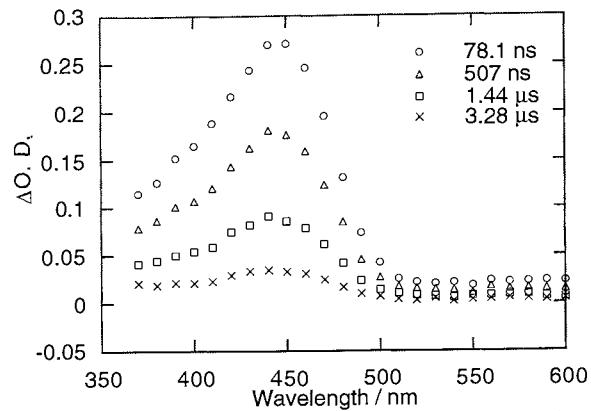


Figure 1. Transient absorption spectra observed on excitation of MS (0.101 M) in the presence of acetophenone (0.102 M) in benzene. Excitation wavelength was 360 nm. Time indicates the delay time after the laser pulse.

energies of the enol form and the observed triplet were estimated.

The triplet energy of the enol form of MS was estimated by observing the rate constant of triplet energy transfer from acetophenone to MS. A triplet-triplet absorption spectra of MS was observed around 450 nm on acetophenone sensitization with 360 nm laser. The rise time of the observed triplet was dependent on the concentration of MS. The rate constant of triplet energy transfer from acetophenone to MS was determined to be 1.1×10^9 M⁻¹ s⁻¹ by observing the rise time of the triplet in the presence of varying amount of MS. Since this value is smaller than the diffusion controlled rate constant ($k_{\text{dif}} = 6.3 \times 10^9$ M⁻¹ s⁻¹),²¹ the energy transfer process should be slightly endothermic. According to the Sandros' equation¹² the above value of k_{q} gave the endothermicity of the energy transfer from acetophenone to MS, ΔE_a , to be 3.8 kJ mol⁻¹. Thus, the triplet excitation energy of MS is 3.8 kJ mol⁻¹ higher than acetophenone and is 314 kJ mol⁻¹. This energy value is also supported by the following reasons: 1) MS was not sensitized by benzophenone ($E_T = 287$ kJ mol⁻¹).²⁰ 2) The triplet energy of methyl benzoate is 326 kJ mol⁻¹.²⁰ 3) The triplet energy of the rotated form, which the phenol hydrogen is bonded to the methoxy oxygen of the ester moiety, is 322 kJ mol⁻¹.¹⁸

$$k_{\text{q}} = k_{\text{dif}} \exp(-\Delta E_a / RT) / [1 + \exp(-\Delta E_a / RT)] \quad (1)$$

The triplet energy of the observed triplet was estimated by observing triplet energy transfer rates from MS triplet to various quenchers. The observed quenching rate constants of MS triplet by various quenchers are shown in Table 1. The rate constant varied with the energies of quenchers. The MS triplet was quenched with the rate constant of ca. 2×10^9 M⁻¹ s⁻¹ by acenaphthene ($E_T = 250$ kJ mol⁻¹)²⁰ and naphthalene ($E_T = 253$ kJ mol⁻¹),²⁰ indicating that these quenching processes are

isoenergetic or slightly endothermic. On the other hand, α -methylstyrene ($E_T = 260 \text{ kJ mol}^{-1}$)²⁰ quenched the MS triplet by $5.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; this process is endothermic by 5.9 kJ mol^{-1} from equation 1. Therefore, the triplet energy of the MS triplet, observed around 450 nm, is calculated as 254 kJ mol^{-1} . In contrast, the quenching rate constant by biphenyl ($E_T = 274 \text{ kJ mol}^{-1}$)²⁰ and triphenylene ($E_T = 280 \text{ kJ mol}^{-1}$)²⁰ are less than $10^8 \text{ M}^{-1} \text{ s}^{-1}$, indicating that these processes are endothermic by greater than 10 kJ mol^{-1} . The observed triplet energy of the transient is close to the value of 240 kJ mol^{-1} reported by Catalán and Díaz in ethyl iodide matrices at 77 K.¹⁶ Thus, the triplet energy of the transient observed is estimated to be 254 kJ mol^{-1} .

Table 1. Quenching rate constants of MS triplet by various triplet quenchers

Quencher	$E_T / \text{kJ mol}^{-1}$	$k_q / 10^9 \text{ M}^{-1} \text{ s}^{-1}$
acenaphthene	250	2.1
naphthalene	253	1.7
α -methylstyrene	260	0.53
biphenyl	274	$< 10^8$
triphenylene	280	$< 10^8$

Those quenching experiments show that 314 kJ mol^{-1} is required to excite the ground state MS to the triplet state, whereas the observed triplet possesses only 254 kJ mol^{-1} over the ground state. This result precludes the two candidates for the assignment of the transient; the enol form and the rotated form. Therefore, we conclude that MS undergoes the hydrogen atom transfer to form the keto form in the triplet state adiabatically (Figure 2). This is the first clear report on the photoinduced hydrogen atom transfer of MS in the triplet state at room temperature.

On direct excitation on 308 nm laser pulse, a weak transient absorption spectra, consisting of two distinguishable components with different lifetime, was observed. Both transients were quenched by oxygen and assigned to the triplet state. The fast decaying component, peaked around 400 nm, decayed with the lifetime of about 100 ns. Since this component was not observed upon triplet sensitization, it might be assigned to the rotated form. The slow decaying component, peaked at 450 nm, decayed with the lifetime of about 4 μs . It was assigned to the triplet state of the keto form because its spectrum and lifetime were similar to the triplet keto form observed on the acetophenone sensitization (vide supra). Thus, the triplet state of the keto form was also formed on the direct excitation. The quantum yield of the formation of the triplet keto form was estimated to be 0.02 in benzene by comparing the intensities of the triplet to triplet absorption with standard compounds. Research focused on the dynamics of the triplet state on the direct excitation is currently in progress.

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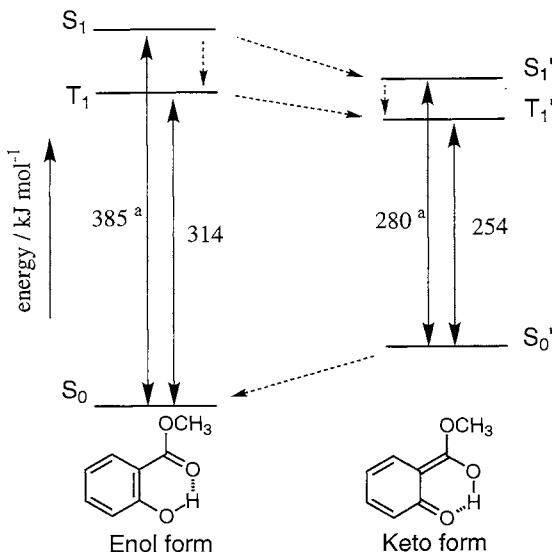


Figure 2. Potential energy diagram of photoinduced hydrogen atom transfer of methyl salicylate. ^aCalculated from absorption and fluorescence spectra.

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- 21 In our experimental condition, benzophenone triplets were quenched by naphthalene with the rate constant of $6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and therefore, the diffusion controlled rate constant (k_{diff}) is estimated as $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.
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